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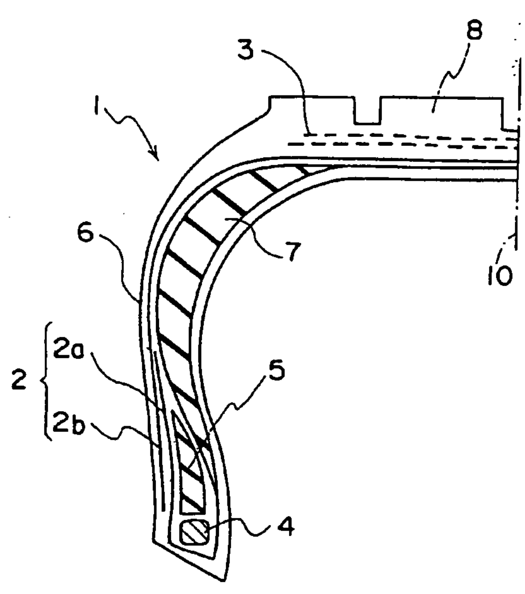
(54) Rubber composition and pneumatic tire using said rubber composition

(57) A rubber composition having excellent heat resistance and a pneumatic tire produced by using this rubber composition are provided.

The rubber composition has, in a curve exhibiting a change in dynamic storage modulus during elevation of temperature, an intersection of an extrapolation line of a portion in which the dynamic storage modulus is approximately constant before rapidly decreasing at temperatures higher than 100°C and an extrapolation line of a portion in which the dynamic storage modulus rapidly decreases, at a temperature of 170°C or higher.

FIG. 1



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A is at least one compound selected from the group consisting of tetramethylolmethane, trimethylolpropane and polymers of these compounds.

(10) A rubber composition described in any of (4), and (6) to (9), wherein the polyhydric alcohol is trimethylolpropane or a dimer of tetramethylolmethane.

(11) A rubber composition described in any of (4), and (6) to (10), wherein the amount of the compound A is 0.5 to 20 parts by weight per 100 parts by weight of a rubber component.

(12) A pneumatic tire comprising side wall portions reinforced with a rubber reinforcing layer, wherein a rubber composition for the rubber reinforcing layer comprises the rubber composition described in any of (1) to (11).

(13) A pneumatic tire comprising bead fillers for which the rubber composition described in any of (1) to (11) is used.

(14) A pneumatic tire described in any of (12) and (13), which is a run-flat tire.

(15) A rubber composition for side reinforcing layers and/or bead fillers comprising sodium 1,6-hexamethylenedithiosulfate dihydrate.

(16) A rubber composition described in (15), which comprises a compound A having two or more ester groups in one molecule.

(17) A rubber composition for side reinforcing layers and/or bead fillers which comprises a compound A having two or more ester groups in one molecule.

(18) Use of sodium 1,6-hexamethylenedithiosulfate dihydrate in side reinforcing layers and/or bead fillers of a pneumatic tire.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] Figure 1 shows a cross-sectional view of an example of the pneumatic tire of the present invention.

[0008] Figure 2 shows a curve exhibiting the change in dynamic storage modulus during elevation of temperature.

[0009] Figure 3 shows a diagram exhibiting, in the curve exhibiting a change in dynamic storage modulus during elevation of temperature, temperature C at an intersection of extrapolation line A of a portion in which the dynamic storage modulus shows an approximately linear change before rapidly decreasing at temperatures higher than 100°C and extrapolation line B of a portion in which the dynamic storage modulus rapidly decreases.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0010] The rubber composition has, in a curve exhibiting the change in dynamic storage modulus E' during elevation of temperature, the intersection of extrapolation line A of a portion in which the dynamic storage modulus shows an approximately linear change before a rapid decrease at temperatures higher than 100°C and extrapolation line B of a portion in which the dynamic storage modulus rapidly decreases, at a temperature of 170°C or higher.

[0011] In the curve exhibiting the change in dynamic storage modulus E' during elevation of temperature, the temperature at the intersection of extrapolation line A of a portion in which the dynamic storage modulus shows an approximately linear change before a rapid decrease at temperatures higher than 100°C and extrapolation line B of a portion in which the dynamic storage modulus rapidly decreases is temperature C shown in Figure 3.

[0012] When the temperature at the intersection is lower than 170°C, durability of the rubber composition at the high temperatures caused by heat generated in the run-flat condition is not sufficient. Therefore, the temperature must be 170°C or higher.

[0013] Extrapolation line A is a line obtained by extrapolation of the portion in which the dynamic modulus shows an approximately linear change before a rapid decrease at temperatures higher than 100°C in the curve exhibiting the change in dynamic storage modulus during elevation of temperature. It is preferable that extrapolation line A contacts the curve showing the change in dynamic storage modulus in a range of 40°C and more preferably in a range of 20°C.

[0014] Extrapolation line B is a line obtained by extrapolation of the portion in which the dynamic modulus rapidly decreases. It is preferable that extrapolation line B contacts the curve showing the change in dynamic storage modulus in a range of 15°C and more preferably in a range of 10°C.

[0015] In the present invention, it is preferable that sodium 1,6-hexamethylenedithiosulfate dihydrate is used as an agent to prevent heat aging. Sodium 1,6-hexamethylenedithiosulfate dihydrate suppresses rupture of chains of the polymer constituting the rubber component. Therefore, in the curve exhibiting the change in dynamic storage modulus during elevation of temperature, the intersection of the extrapolation line A of the portion in which the dynamic modulus shows an approximately linear change before a rapid decrease at temperatures higher than 100°C and the extrapolation line B of the portion in which the dynamic modulus rapidly decreases can be easily brought to a temperature of 170°C or higher.

[0016] The amount of sodium 1,6-hexamethylenedithiosulfate dihydrate is not particularly limited. From the standpoint of achieving the object of the present invention, it is preferable that the amount is in the range of 1 to 10 parts by weight per 100 parts by weight of the rubber component.

reinforcing layers 7 having a crescent-shaped cross section are disposed at the inner circumferential surface of the side walls portion of the turned-up carcass ply 2a.

[0030] It is preferable that at least one of the rubber composition for the bead filler and for the rubber reinforcing layer comprises sodium 1,6-hexamethylenedithiosulfate dihydrate. It is more preferable that the rubber composition for the bead filler further comprises a compound having two or more ester groups in one molecule. The rubber composition for the bead filler and/or the rubber reinforcing layer preferably has a dynamic storage modulus E' of 8 MPa or more at 160°C, more preferably 10 MPa or more at 160°C and most preferably 13 MPa or more at 160°C.

[0031] The best tire durability may be obtained when both of the rubber members comprise the above described rubber composition.

[0032] When conventional pneumatic tires are used in a condition of a markedly reduced inner pressure (in the so-called run-flat condition), deformation of the tire caused by the load markedly increases. Heat generation caused by the deformation increases particularly markedly at side wall portions and damage occurs in the side wall portions. This problem of conventional tires can be overcome by the pneumatic tire comprising the above rubber composition.

[0033] Thus, durability of the tire side wall portions can be particularly improved by using the compound described in the present invention in the rubber compositions for the tire and preferably in the rubber compositions for the rubber reinforcing layer of the side wall portions and/or the bead fillers. As the result, for example, the driving distance in the run-flat condition can be remarkably increased. In other words, the present invention can be effectively applied to the run-flat tire which particularly emphasizes safety in the run-flat condition.

EXAMPLES

[0034] The present invention will be described specifically with reference to examples in the following. However, the present invention is not limited by the examples.

[0035] In the examples, part and % mean part by weight and % by weight unless otherwise mentioned.

[0036] Various measurements were made in accordance with the following methods.

(1) Viscoelastic characteristics of a rubber composition

[0037] A slab sheet having a thickness of 2 mm was prepared by vulcanization at 160°C for 12 minutes and a sample having a width of 5 mm and a length of 20 mm was cut out from the slab sheet. Dynamic storage modulus (E') of the sample was measured using SPECTROMETER manufactured by TOYO SEIKI Co., Ltd. at an initial load of 160 g under a dynamic strain of 1% at a frequency of 52 Hz while the temperature was raised from 20 to 250°C at a rate of 3°C/second.

(2) Durability of a tire in the run-flat condition

[0038] A tire inflated with an inner pressure of 3.0 kg/cm^2 was fitted to a rim. After the tire was left standing at a room temperature of 38°C for 24 hours, the pressure inside the tire was set to the atmospheric pressure by removing the valve core. Then, the tire was subjected to the drum test under a load of 570 kg at a speed of 89 km/hour at a temperature of 38°C. The distance driven before trouble occurred was taken as durability in the run-flat condition. Durabilities in the run-flat condition in the Examples are expressed as indices relative to the durability of the control tire in Comparative Example 1 which is set at the value of 100. The greater the index, the better the durability in the run-flat condition.

Examples 1-18:

[0039] Rubber compositions were prepared in accordance with the formulations shown in Table 1 and the dynamic storage modulus E' was measured with an elevation of temperature. The results are shown in Table 1.

Table 1 - 1

Example		1	2	3	4	5	6
Comparative Example	1						
Natural rubber	30.0	30.0	30.0	30.0	30.0	30.0	30.0
Butadiene rubber *1	70.0	70.0	70.0	70.0	70.0	70.0	70.0
Carbon black *2	60.0	60.0	60.0	60.0	60.0	60.0	70.0
Softener *3	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Zinc oxide	3.0	3.0	3.0	3.0	3.0	3.0	3.0

Table 1 - 3 (continued)

Example	13	14	15	16	17	18
Butadiene rubber *1	70.0	70.0	70.0	70.0	70.0	70.0
Carbon black *2	60.0	60.0	60.0	60.0	60.0	60.0
Softener *3	5.0	5.0	5.0	5.0	5.0	5.0
Zinc oxide	3.0	3.0	3.0	3.0	3.0	3.0
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0
Antioxidant *4	2.0	2.0	2.0	2.0	2.0	2.0
Vulcanization accelerator *5	3.5	3.5	3.5	3.5	3.5	3.5
Agent for preventing heat aging *6	2.0	3.0	5.0	10.0	3.0	5.0
Agent for preventing degradation *7	5.0	5.0	5.0	5.0	0.0	0.0
Sulfur	5.0	5.0	5.0	5.0	5.0	5.0
Temperature C (°C)	175	178	180	180	178	178
ΔE' *8 (MPa)	2.5	2.5	2.5	2.5	3.0	3.0
Applied portion						
reinforcing rubber	applied	applied	applied	applied	applied	applied
bead filler	not applied	not applied	not applied	not applied	applied	applied
Durability in the run-flat condition	134	142	154	166	143	150

The amounts in the above table are all in parts by weight
*1: BR01 (a trade mark; manufactured by JSR Corporation)
*2: FEF
*3: Spindle oil
*4: NOCRAC 6C (a trade mark; manufactured by OUCHI SHINKO KAGAKU KOGYO Co., Ltd.)
*5: NOCCELOR NS (a trade mark; manufactured by OUCHI SHINKO KAGAKU KOGYO Co., Ltd.)
*6: Sodium 1,6-hexamethylenedithiosulfate dihydrate
*7: KAYARAD D310 (a trade mark; manufactured by NIPPON KAYAKU Co., Ltd.)
*8: Range of the change in storage modulus in the temperature range of 170 to 200°C

[0040] As shown in Table 1, the rubber composition of the present invention comprising the agent for preventing heat aging had, in the curve exhibiting the change in dynamic storage modulus during elevation of temperature, the intersection of the extrapolation line A of the portion in which the dynamic storage modulus shows an approximately linear change before rapidly decreasing at temperatures higher than 100°C and the extrapolation line B of the portion in which the dynamic storage modulus rapidly decreases, at a temperature of 170°C or higher independently of the type of the rubber component and the amount of carbon black. In Examples 12 to 16 in which the agent for preventing degradation was used in combination, the change in the dynamic storage modulus with temperature in the temperature range of 170 to 200°C decreased.

[0041] Radial tires having a size 225/60R16 were prepared in accordance with a conventional process using the above rubber compositions as the rubber composition for the rubber reinforcing layers disposed at the side wall portions and were subjected to the durability test. The results are shown in Table 1. In Examples 17 and 18 shown in Table 1, the same rubber compositions were used for the rubber reinforcing layers and for the bead fillers.

[0042] As shown by the results in Table 1, durability in the run-flat condition can be improved by using the rubber composition of the present invention as the rubber composition for the rubber reinforcing layers. As shown by the results of Examples 17 and 18, durability of the tire in the run-flat durability can be further improved by using the rubber composition of the present invention as the rubber compositions for the rubber reinforcing layers and for the bead fillers.

Examples 19-24:

[0043] Rubber compositions were prepared in accordance with the formulations shown in Table 2 and the dynamic storage modulus E' was measured with an elevation of temperature. The results are shown in Table 2.

3. A rubber composition according to claim 1 or 2, wherein the amount of sodium 1,6-hexamethylenedithiosulfate dihydrate is 1 tolO parts by weight per 100 parts by weight of a rubber component.

4. A rubber composition according to any one of claims 1 to 3, comprising a compound A having two or more ester groups in one molecule.

5. A rubber composition having, in a curve exhibiting a change in dynamic storage modulus during elevation of temperature, a difference $\Delta E'$ between the maximum value and the minimum value of the dynamic storage modulus at a temperature between 180 and 200°C of 2.5 MPa or less.

6. A rubber composition according to claim 5, comprising a compound A having two or more ester groups in one molecule.

7. A rubber composition according to claim 4 or 6, wherein the compound A is an acrylate or a methacrylate.

8. A rubber composition according to any one of claims 4, 6 and 7, wherein the compound A is a polyfunctional ester of a polyhydric alcohol and acrylic acid or methacrylic acid.

9. A rubber composition according to any one of claims 4, and 6 to 8, wherein the polyhydric alcohol forming the compound A is at least one compound selected from the group consisting of tetramethylolmethane, trimethylolpropane and polymers of these compounds.

10. A rubber composition according to any one of claims 4, and 6 to 9, wherein the polyhydric alcohol is trimethylolpropane or a dimer of tetramethylolmethane.

11. A rubber composition according to any one of claims 4, and 6 to 10, wherein the amount of the compound A is 0.5 to 20 parts by weight per 100 parts by weight of a rubber component.

12. A pneumatic tire comprising side wall portions reinforced with a rubber reinforcing layer, wherein a rubber composition for the rubber reinforcing layer comprises the rubber composition according to any one of claims 1 to 11.

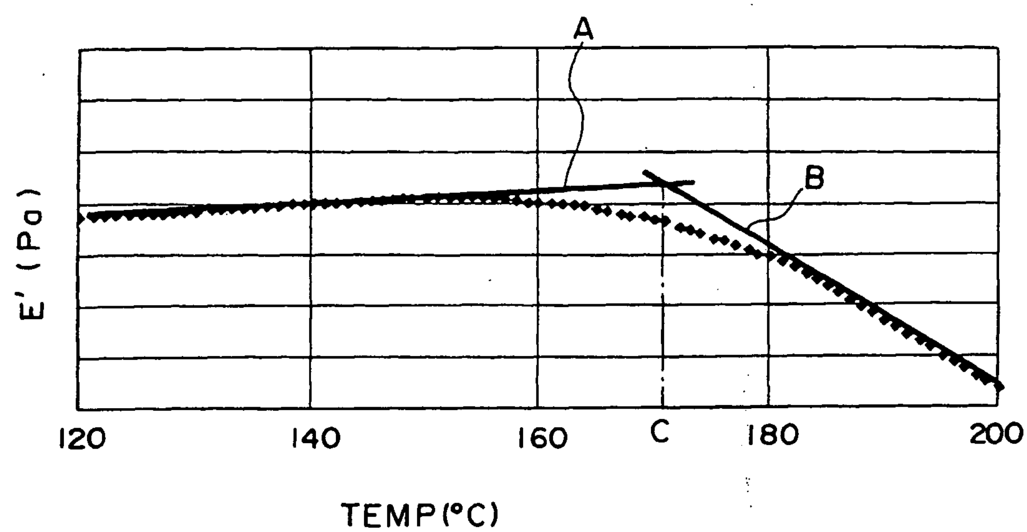
13. A pneumatic tire comprising bead fillers for which the rubber composition according to any one of claims 1 to 11 is used.

14. A pneumatic tire according to claim 12 or 13, which is a run-flat tire.

15. A rubber composition for side reinforcing layers and/or bead fillers comprising sodium 1,6-hexamethylenedithiosulfate dihydrate.

16. A rubber composition according to claim 15, comprising a compound A having two or more ester groups in one molecule.

FIG. 3



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(57) A rubber composition having excellent heat resistance and a pneumatic tire produced by using this rubber composition are provided.

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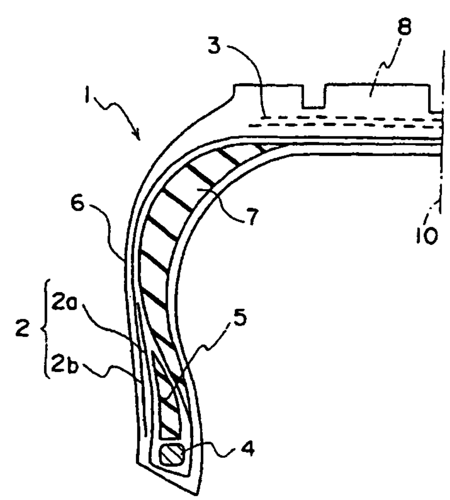
FIG. 1



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